Time-Averaged Fluxes of Lead and Fallout Radionuclides to Sediments in Florida Bay

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The Problem

Florida Bay, located at the southern end of the Florida peninsula (Fig. 1), is part of an ecosystem that encompasses the southern half of the state, including the Everglades, Florida Keys, and reef tract. Recent ecological change in the Bay, including occurrences of elevated salinity, widespread sea grass mortality, eutrophication, contamination and declines of faunal populations, have been of concern to the general public and specific interest groups. A comprehensive federal and state program was initiated to remedy such ecosystem deterioration and an interagency group has identified research needed to address management issues. Included among research priorities was the need to know the relationship between biota and environmental changes during the past 150 years. The ecological status of the Bay during the first half of this century is known only anecdotally, with sporadic documentation in the 1960s. Ecological assessments and salinity measurements became routine only in the 1970s. So reconstructing ecosystem conditions during this century from sediment cores or other archival records is critical for determining the effects of previous human impacts and for predicting consequences of future actions.

The Approach

A multi-institutional study was initiated in 1994 to determine whether the uranium-series radionuclides ^{210}Pb and ^{226}Ra could be used to establish sediment core chronologies spanning the past 100 years. The method is widely used in lacustrine and coastal marine environments to obtain rates of sediment accumulation, as well as depths and rates of near-surface mixing of sediments. To validate the method, sediment distributions of stable lead were compared with a previously determined time-series record of lead in banded coral *Montastrea annularis* located on the ocean side of the Keys (Fig. 1). In addition, sediment profiles of lead, as well as fallout ^{137}Cs and plutonium isotopes (Pu), were compared with the time-dependence of well-characterized atmospheric delivery rates.

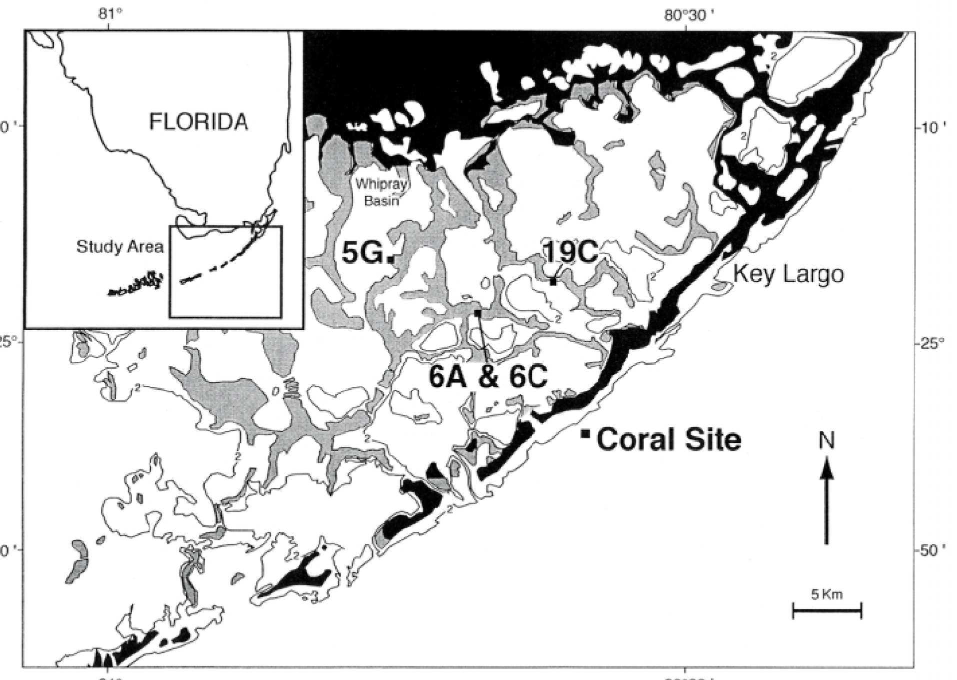

Figure 1. Florida (inset) and the Florida Bay region. Cores were collected from mudbanks (lightly shaded areas) adjacent to Whipray Basin (5), from Bob Allen Bank (6), and Russell Bank (19). Dark regions indicate islands or mainland. Specimens of coral (*M. Annularis*) analyzed for lead by others were collected at the indicated ocean-side site near Plantation Key.

Sediments of Florida Bay

Sediments have been accumulating in Florida Bay for about 4000 years since wetland flooding during the last stages of Holocene sea-level rise. Holocene sediments form a network of mud banks and islands, partitioning the Bay into more than 30 small basins, each 1 to 4 meters deep and up to a few kilometers wide. Sediments consist mainly of sand, silt- and clay-size carbonate particles ("muds") and peats, both produced by organisms in the Bay. Although the shallow bay is frequently impacted by tropical storms and hurricanes, and by populations of benthic infauna, there are promising locales where undisturbed sediments needed for radiometric dating may be found.

Sediment Coring

Sediment cores for this study were collected from Whipray Basin, two from Bob Allen Bank, and one from Russell Bank (Fig. 1) by one or more of our illustrious team members, some of whom are shown in Fig. 2. All sites were located on southern, accreting sides of mudbanks. Specific cores were selected to maximize geochronological precision and accuracy, and are likely not typical of most recent deposits in the Bay. Sediment surfaces at Whipray (5G) and Bob Allen (6A) were densely covered with saw grass, Thalassia testudinum, while cores at Bob Allen (6c) and Russell Bank (19C) were grass-free. Cores up to 2 m long, were taken in May 1994 (5G, 6A and 6C) and February 1995 (19C) using a 6-meter pontoon barge (Fig. 3) equipped with a moon pool and piston coring equipment. Cores were taken to local hospitals for X-radiography on the evening of each collection day, then hydraulically extruded and sectioned into two-cm intervals.

Sediment core dating using ^{210}Pb and ^{226}Ra

The source of ^{210}Pb is the long-lived radionuclide ^{226}Ra that occurs widely in crustal rocks and soils. Decay of ^{226}Ra produces the short-lived, unreactive gas ^{222}Rn, some of which escapes from mineral matrices into the atmosphere and decays through a series of extremely short-lived progeny to long-lived ^{210}Pb. This generalized pathway is shown here:

$$\underset{[soil\,/\,rocks]}{^{226}Ra(t_{1/2}=1600yr)} \rightarrow \underset{[air]}{^{222}Rn(t_{1/2}=3.8days)} \rightarrow \underset{[air\,/\,rain]}{^{210}Pb(t_{1/2}=22.3yr)}$$

Figure 2. Photos of some of our dedicated colleagues. Top (left to right): Dave Rudnick, Chuck Holmes, Bob Halley. Bottom: Mike Bothner, Marci Marot, and Gene Shinn.

Figure 3. Pontoon boat (USGS) with tripod rigging for collection of piston cores through a moon pool.

Once formed, ^{210}Pb is rapidly removed from the air by precipitation and dry deposition and, when delivered to most lakes and coastal waters, is rapidly transferred to sediments. In Florida Bay, ^{210}Pb enters mainly through this atmospheric route. However other potential sources to this system include dissolved ^{226}Ra in ocean water, runoff of ^{210}Pb and ^{226}Ra from the (Everglades) and upward migration of ^{226}Ra- and ^{222}Rn-enriched waters through porous limestone/peat deposits underlying recent sediments in the Bay.

Sediment chronologies are based on constant net rates of supply to sediments of excess ^{210}Pb, Fo (dpm cm^{-2} yr^{-1}), and mass, rs (g cm^{-2} yr^{-1}). Excess ^{210}Pb activity (dpm g^{-1}), defined as the difference between total ^{210}Pb and ^{226}Ra, is calculated as,

$$A_{ex}(g) + \frac{F_o}{r_s} e^{-\lambda g / r_s} \qquad (1)$$

where g (g cm^{-2}) is the cumulative weight of sediment at a given depth, and λ is the radioactive decay constant ($0.69315/t_{1/2} = 0.03114\ yr^{-1}$). Equation 1, which automatically takes account of sediment compaction, implies no post-depositional radionuclide mobility or sediment mixing.

Sediment Chronologies from ^{210}Pb and ^{226}Ra

Vertical profiles (Fig. 4) show that total ^{210}Pb (solid black circles) is significantly higher than ^{226}Ra (solid orange circles) in near-surface sediments and approaches (secular) equilibrium with depth. Significant ^{210}Pb background activity is due to decay of ^{226}Ra naturally present in sediment minerals. In core 5G from Whipray Basin, a pronounced upward excursion in total ^{210}Pb activity occurs in the bottom 8 cm of the core where basal peat overlies porous Pleistocene limestone deposits in contact with radium-rich groundwater. Excess ^{210}Pb activities (^{210}Pb minus ^{226}Ra, solid blue circles) plotted versus cumulative sediment weight (Fig. 5), illustrate the generally excellent agreement between observed excess ^{210}Pb profiles and the above simple exponential model (red lines). Values of the mass accumulation rate, rs, vary more than five-fold among sites. Sediment ages (years b.p.) are calculated as g/rs . Shown in Fig. 6 are age-depth relations based on mass accumulation rates (red lines) with uncertainty envelopes of ± 2 standard deviations (dashed blue lines).

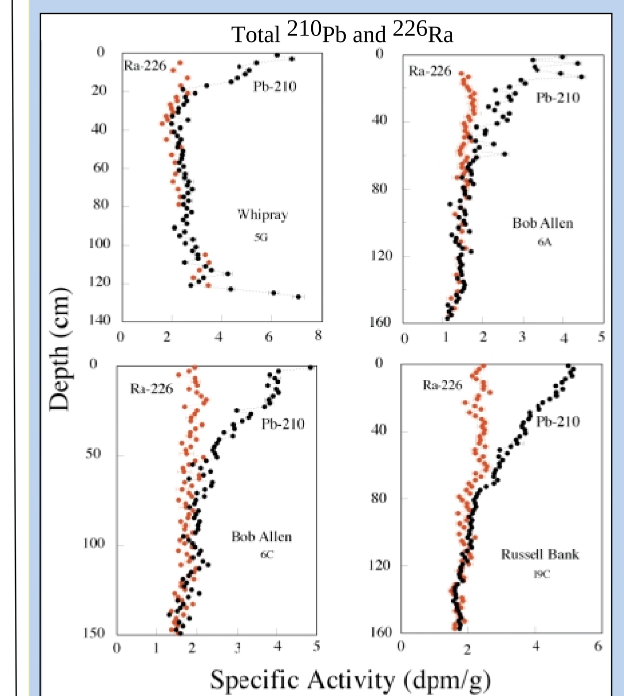

Figure 4. Total ^{210}Pb (solid black circles) and ^{226}Ra (solid orange circles). ^{210}Pb activities exceed ^{226}Ra (by ca. 2x) in near-surface sediments and approach secular equilibrium with increasing depth.

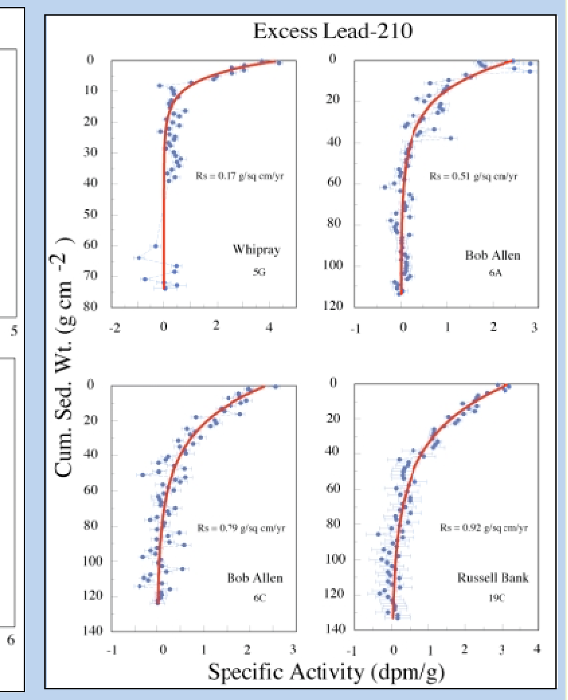

Figure 5. Excess ^{210}Pb versus cumulative dry weight of sediment. Exponential model (Eq. 1) profiles are shown as solid red lines. Mean accumulation rates vary more than five-fold among cores and are determined with greatest precision in two cores from grass-free sites (6C and 19C).

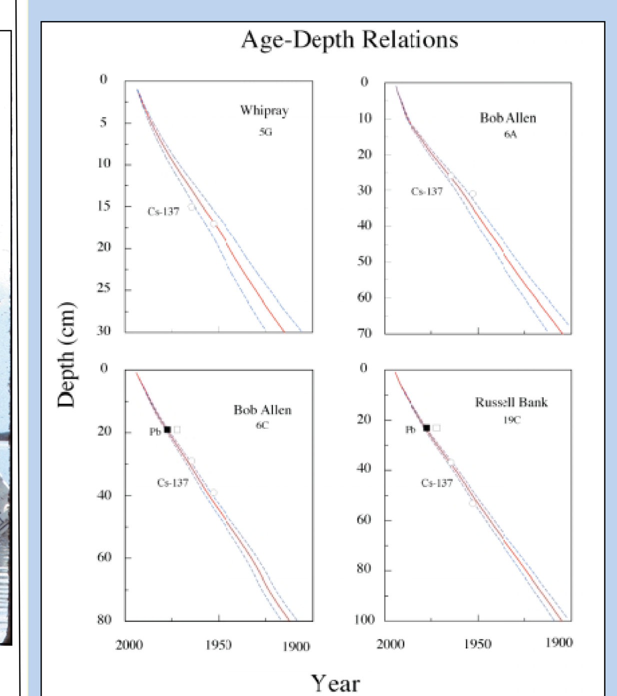

Figure 6. Age-depth relations (solid red line) with uncertainty (± 2 standard deviations) envelopes (dashed blue lines) based on ^{210}Pb. Assignment of dates (1952 and 1964) to depth of horizon (onset) and peak in ^{137}Cs profiles, respectively, agree satisfactorily with ^{210}Pb dates (open circles). Assignments of 1978 (coral lead peak) to lead peaks in cores 6C and 19C also agree with ^{210}Pb dates (dark squares); assignments of 1972 (continental atmospheric lead peak) do not (open squares).

Comparison of Lead in Dated Sediments and Annual Coral Bands

Time-series records of lead in sediment cores 6A, 6C, and 19C, and in layers of annually-banded coral, M. annularis are compared in Fig. 7. Sediment lead records (solid black circles) are consistent among sites, although the near-surface record is incomplete for core 6A. In coral layers, Pb/Ca ratios (solid green squares) are in excellent accord with the sediment records. In cores 6C and 19C, lead maxima occur at 1978 ± 2 years in accord with prior observation of a six year lag between peak atmospheric lead in 1972 and maximum coral lead. Also excess Pb/ excess ^{210}Pb ratios are comparable in coral and sediment samples of the same age. In 1982, the coral sample collection year, the ratio was 0.33 µg/dpm compared with an average ratio in 1982 of 0.37 ± 0.09 µg Pb/dpm in cores 6A, 6C and 19C. Evidently the atmosphere is the primary source of lead species (both Pb and ^{210}Pb), which are delivered to sediments and coral. Both media accumulate lead species in proportion to their concentrations in ambient waters despite differences in principal modes of incorporation, i.e. particle scavenging versus coral lattice-binding of dissolved Pb. The excellent agreement between sediment and coral Pb records confirms the ^{210}Pb chronology.

Sediments and Coral as Recorders of Lead and Fallout ^{137}Cs Loading to Florida Bay

Although coral and sediment lead records agree nicely, how well do these media record the history of a principally atmospheric loading of lead to the south Florida ecosystem? And how good is the agreement between time-series records of atmospheric deposition and sedimentary concentrations of ^{137}Cs and Pu? Lead deposition over the bay, represented by atmospheric concentration data for the continental U.S. (Fig. 8, lower panel, solid violet line), is compared with the consumption of lead in gasoline (dashed blue line). After about 1950, this is the principal source of atmospheric lead over the U.S. For ^{137}Cs ($t_{1/2}$ = 30.2 yr), originating from atmospheric testing of nuclear weapons, rates of deposition in the Miami area are quite well known from monthly measurements made over many years. The record is shown in the top panel of Fig. 8 (green curve). Deposition of Pu isotopes, principally ^{239}Pu ($t_{1/2}$ = 24,400 yr) and ^{240}Pu ($t_{1/2}$ = 6600 yr), is essentially proportional to the ^{137}Cs deposition rate.

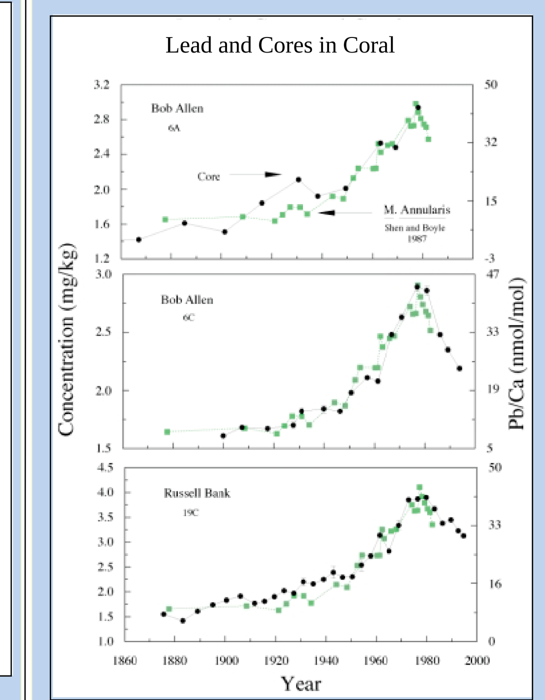

Figure 7. Concentrations of lead in cores 6A, 6C, and 19C (solid black circles) versus ^{210}Pb dates. Molar ratios of Pb/Ca in annual layers of *M. Annularis* (solid green squares) versus coral layer ages. The good agreement demonstrates the validity of $^{210}Pb/^{226}Ra$ dating.

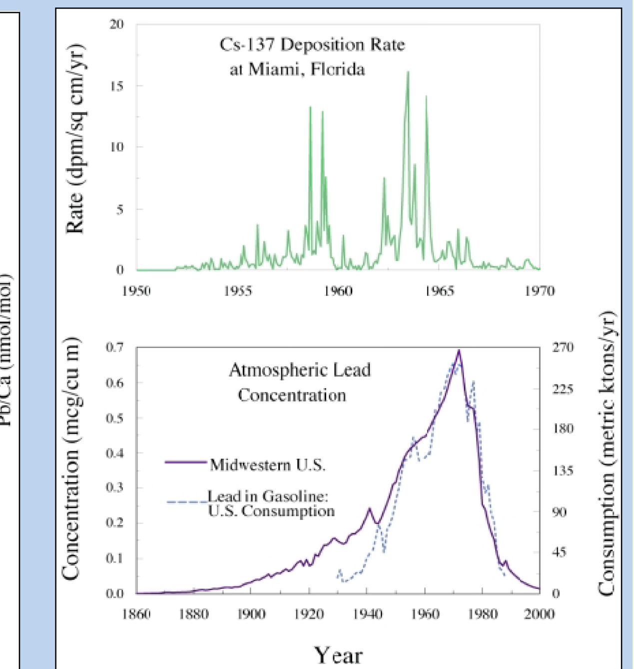

Figure 8. (top) Record of ^{137}Cs deposition at Miami. This (source) function has been used to calculate STA model (Eq. 2) profiles of ^{137}Cs in cores. (bottom) Generalized record of non-urban atmospheric lead concentrations in the continental U.S. (solid violet line). This source function is used to calculate STA model profiles of lead in sediments and coral. Annual U.S. consumption of lead in gasoline between 1930 and 1988 is compared (dashed blue curve).

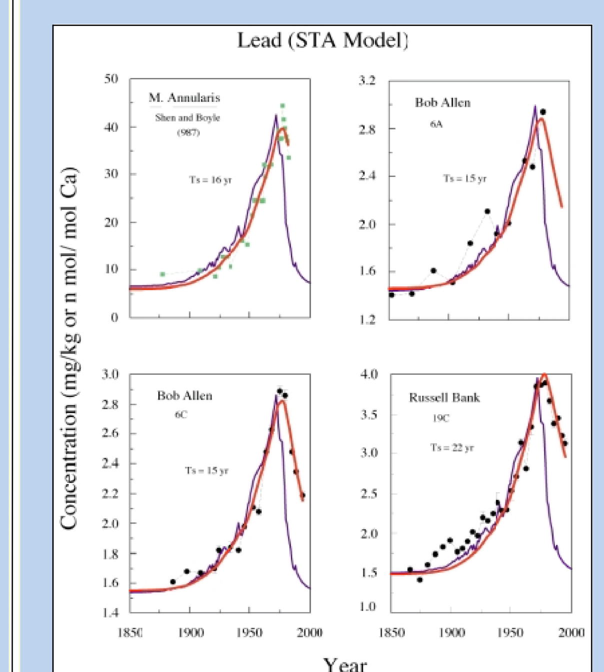

Figure 9. (Upper left panel). Pb/Ca molar ratio in *M. Annularis* (solid green squares). (Other panels). Profiles of lead (solid black circles) versus ^{210}Pb dates. The violet lines represent the continental lead source function. Red lines are optimized STA model results for the indicated residence times.

Concentrations of lead in coral (Fig. 9, top left panel, solid green squares) and in sediment cores 6A,6C and 19C (Fig. 9, remaining panels, solid black circles), mismatch the atmospheric fallout record (violet curves). The mismatch is mainly that the peak atmospheric concentration (in 1972) occurs six years earlier than the peak (1978) in the coral and sediment records. The mismatch between the sediment ^{137}Cs records and atmospheric fallout is even more pronounced. In all four cores (Fig. 10) decay-corrected ^{137}Cs profiles (solid black circles) and the fallout record (shaded green areas) are plotted versus year based on ^{210}Pb. The main mismatch here is that the activity of ^{137}Cs persists in sediments long after atmospheric inputs have ceased and the decline in activity is essentially exponential. This is also true for Pu (Fig. 11) where average activities in 6-cm composites (black squares) are shown along with the ^{137}Cs fallout record (shaded green area).

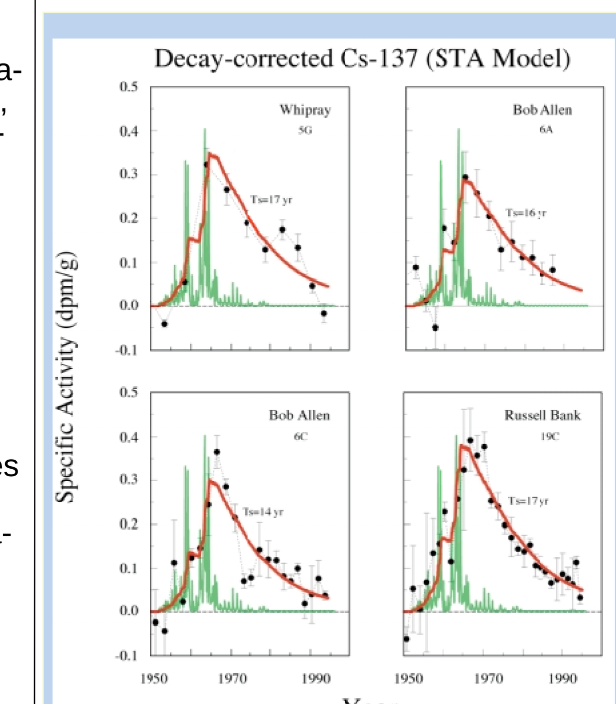

Figure 10. Distributions of ^{137}Cs corrected for radioactive decay. Red lines are optimized STA model results for the indicated residence times. Green lines are temporal records of atmospheric fallout of ^{137}Cs.

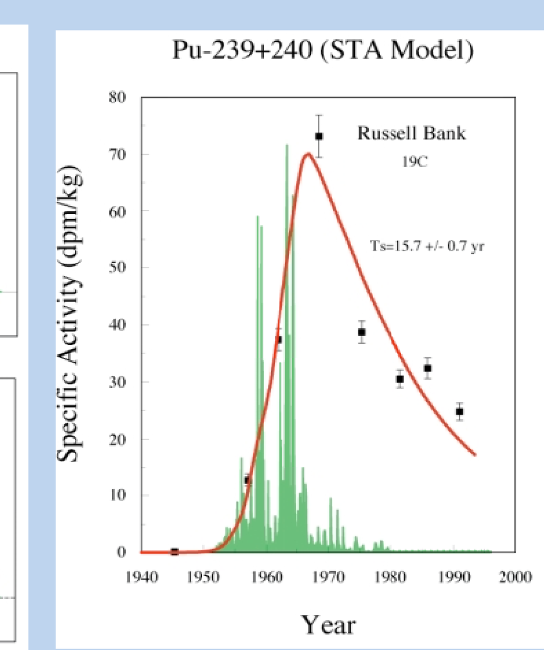

Figure 11. Profile of Pu isotopes ($^{239+240}Pu$) in composite sections of core 19C (solid black squares). Green line is the Pu fallout taken as proportional to the ^{137}Cs fallout record. The red lines is an optimized STA model results for the indicated residence time.

Time-averaging of Atmospheric Lead and Fallout Radionuclides Prior to their Accumulation in Sediments

The likely cause of peak lags in lead and post-fallout persistence of ^{137}Cs and Pu in sediments is that these constituents are not transferred from air to sediment directly. Instead, they enter a sedimentary reservoir, are mixed with prior contributions, resuspended, horizontally dispersed, and re-supplied to sediments including un-mixed deposits selected for this study. Since time averaging is likely accomplished on a Bay- wide scale "outside" our coring sites, we have termed the process "system time averaging". It may be represented in terms of a first-order STA model equation:

$$dF_s / dt = \lambda_s F_a - [\lambda_s + \lambda] F_s \qquad (2)$$

where F_a is the atmospheric flux of lead or ^{137}Cs, F_s is the flux from the reservoir, $\lambda = \ln 2/t_{1/2}$ and $\lambda_s = 1/T_s$ where T_s is the residence time (of particles) in the reservoir. Concentrations of lead, ^{137}Cs and Pu in receptor media are proportional to F_s.

The results of applying the STA model to the lead data, results in the red curves shown in Fig. 9. Time averaging produces the six-year peak lag. Derived reservoir time constants in each case are quite consistent, averaging 19 ± 3 years for sedimentary lead compared with 16 ± 2 years for coral lead. Applied to the ^{137}Cs data, the STA model accounts well for each entire profile (Fig. 10, red lines), and especially the post-fallout exponential decline. The reservoir time constant is essentially the same for all sites, averaging 16 ± 1 year and accords with the 15.7 ± 0.7 year value for Pu (Fig. 11, red line).

Conclusions

Chronologies spanning 70-90 years of recent undisturbed sediment from the mudbanks in central Florida Bay can be established by measuring vertical distributions of ^{210}Pb and ^{226}Ra in X-radiographically evaluated cores from carefully selected sites.

Chronologies were confirmed by the excellent agreement between temporal records of stable Pb in ^{210}Pb-dated sediments and Pb/Ca ratios in annual layers of coral located on the ocean side of the Florida Keys.

Primarily delivered from the atmosphere, Pb, excess ^{210}Pb, ^{137}Cs and Pu subsequently move and are co-deposited with fine particles in the Bay.

Sediments and coral accumulate lead species in proportion to concentrations in ambient waters despite differences in principal modes of incorporation, i.e. particle scavenging versus coral lattice binding of dissolved Pb, respectively.

Distributions of lead and radionuclides can be quantitatively described by a system time averaging (STA) model in which particles, carrying these trace constituents, are mixed in a reservoir with a characteristic (residence) time before re-supply to sediments or coral.

The STA model yields remarkably consistent estimates of particle residence times independent of element, loading history, or archiving medium: for sediment ^{137}Cs, 16; Pu, 15.7; Pb, 19 ; and for coral Pb, 16 years.

Time-averaging could occur largely within the Bay itself where mudbanks build through cycles of particle resuspension, horizontal transport, and redeposition on near-surface sediments subject widely to biological and physical mixing.

The 16-year mean residence time of particles in the reservoir of resuspendable sediments ensures that significant levels of particle-associated, non-degradable contaminants like lead and nuclear fallout will persist for decades following cessation of loads to Florida Bay and the coastal ocean near the Keys.

An STA analysis of sediment radionuclide profiles, published by others, suggests that decade-scale time averaging may be a general feature of coastal marine sedimentary environments.

If so, observations of decade-scale declines in concentrations of key tracers in non-coastal, pelagic regions of the ocean may constitute prima facie evidence for cross-margin transport of materials from coastal sources.

This study will stimulate multi-institutional, interdisciplinary efforts to chronicle ecosystem changes in Florida Bay due to anthropogenic insults that have occurred during the past century.

Acknowledgements
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